

## SYMPOSIUM ON SOLVENT EXTRACTION IN THE ANALYSIS OF METALS

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### INTRODUCTION

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In recent years the analytical chemist has seen the increasing complexity of the problems he is asked to solve keep pace with the spectacular advances in instrumental development of more discriminating methods, so that he is still vitally interested in separations processes. Among separations methods, solvent extraction enjoys a vantage position because of its speed, convenience, applicability to both trace and macro concentration levels and, in a large number of cases, because the extracted constituent of interest is transformed into a readily measured state.

Solvent extraction has been particularly helpful in the analysis of metals and a great many extraction procedures have been utilized by analysts. These procedures may be classified according to the nature of the extractable species formed as either "chelate" or "ion association" extractions.

The extraction process may be conveniently depicted as involving three

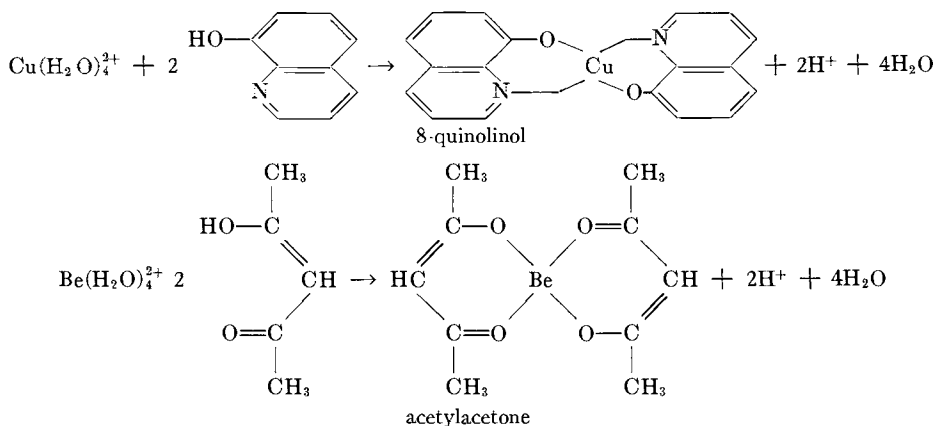
stages: (1) Formation of an extractable species in the aqueous phase, (2) distribution of the extractable species between the two phases, and (3) chemical interactions of the species in the organic phase. With this guide to extraction, attention is focused on the need for complex formation in metals extraction.

Most metal salts are soluble in aqueous media but not particularly so in organic solvents. This may be taken to reflect the affinity of water for the metal ion as shown by the fact that metal ions are hydrated (that is  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ ,  $\text{Cu}(\text{H}_2\text{O})_4^{2+}$  etc.) as well as the natural advantage of water as a solvent with a high dielectric constant. The problems attending the formation of an extractable species in many cases can be related to replacing the water bonded to the metal ion by groups which are less hydrophilic and which would make the resultant species more compatible with organic solvents.

Such groups may be introduced by chelating reagents such as 8-quinolinol or acetylacetone, giving rise to uncharged, organic-soluble, chelates, for example:

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TABLE I.—METAL EXTRACTION SYSTEMS<sup>a</sup>

	Reactive Grouping
<b>I. CHELATE SYSTEMS</b>	
A. 4-membered ring systems	
1. Dialkylthiocarbamates . . . . .	—N—C—S—(—)
2. Xanthates . . . . .	—S=C—S—(—)
B. 5-membered ring systems	
1. <i>N</i> -Benzoylphenylhydroxylamine . . . . .	—O=C—N—O—(—)
2. Cupferron . . . . .	—O=N—N—O—(—)
3. $\alpha$ -dioximes . . . . .	—N=C—C=N—(—)
4. Dithizone . . . . .	—N=N=C—S—(—)
5. 8-quinolinols . . . . .	—N=C—C—O—(—)
6. Toluene-3,4-dithiol . . . . .	(—)S—C=C—S—(—)
7. Catechol . . . . .	(—)O—C=C—O—(—)
C. 6-membered ring systems	
1. $\beta$ -diketones and hydroxycarbonyls . . . . .	—O=C—C=C—O—(—)
(a) Acetylacetone	
(b) Thenoyltrifluoroacetone (TTA)	
(c) Morin	
(d) Quinalizarin	
2. Nitrosonaphthols . . . . .	—O=N—C=C—O—(—)
3. Salicylaldoxime . . . . .	—N=C—C=C—O—(—)
D. Polydentate systems	
1. Pyridyl-azo-naphthol (PAN) . . . . .	—N=C—N=N—C=C—O—(—)

**II. ION ASSOCIATION SYSTEMS**

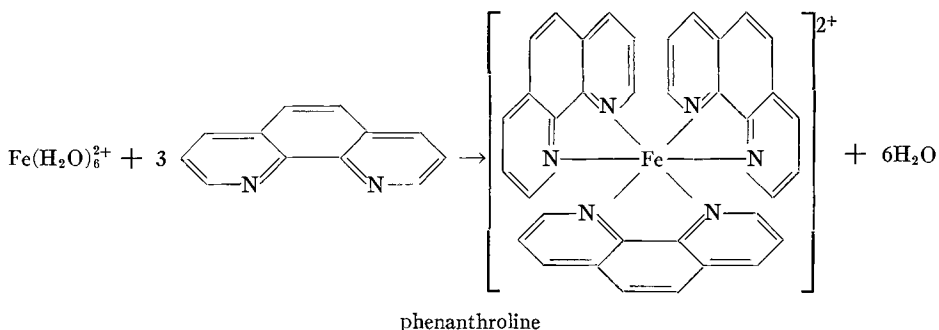
- A. Metal contained in cationic member of ion-pair
1. Alkylphosphoric acids
  2. Carboxylic acids
  3. Cationic chelates
    - a. Phenanthrolines
    - b. Polypyridyls
  4. Nitrate
  5. Trialkylphosphine oxides
- B. Metal contained in anionic member of ion-pair<sup>b</sup>
1. Halides ( $\text{GaCl}_4^-$ )
  2. Thiocyanates ( $\text{Co}(\text{CNS})_4^-$ )
  3. Oxyanions ( $\text{MnO}_4^-$ )
  4. Anionic chelates ( $\text{Co}(\text{Nitroso R salt})_3^{3-}$ )

<sup>a</sup> G. H. Morrison, and H. Freiser, *Analytical Chemistry*, Vol. 30, p. 632 (1958).<sup>b</sup> The cation member associated with these metal-containing anions is usually of an "onium" type such as (a) oxonium, for example,  $\text{ROH}_2^+$ ,  $\text{R}_2\text{OH}^+$ ,  $\text{R}_2\text{COH}^+$  (b) ammonium, for example,  $\text{RNH}_3^+$ , . . .  $\text{R}_4\text{N}^+$ , (c) arsonium,  $\text{R}_4\text{As}^+$  (d) phosphonium,  $\text{R}_4\text{P}^+$  (e) stibonium,  $\text{R}_4\text{Sb}^+$  (f) sulfonium,  $\text{R}_3\text{S}^+$ .

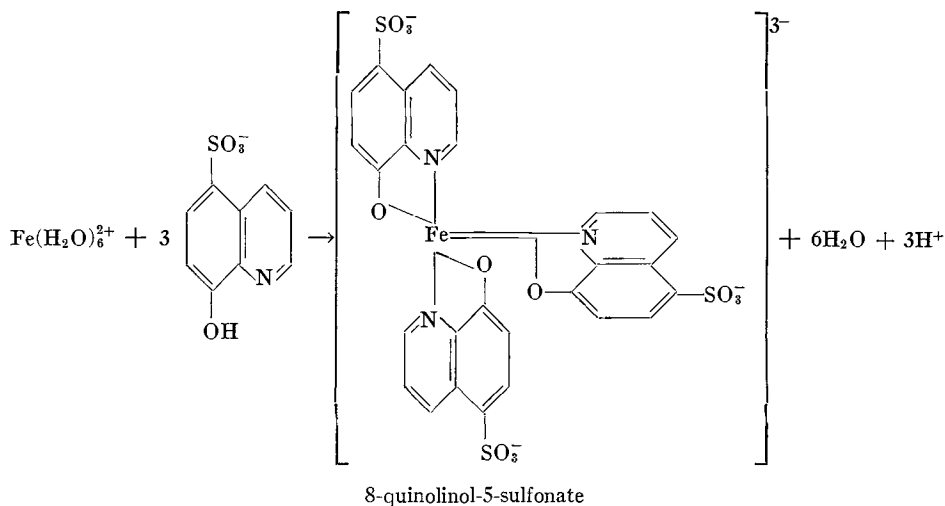
A systematic grouping of chelating agents that have been used in this manner is shown in the first part of Table I.

Not all chelating agents give rise to uncharged metal chelates. However the resulting charged complex has served to remove the waters of hydration of the metal ion, and substitute these by organic groups to give large ions of the following types:

*cationic*



or *anionic*



These ions may form a neutral extractable species by associating with an oppositely charged ion. The neutral species formed by the pairing of oppositely

charged species through simple electrostatic attraction is termed an "ion-association" complex.

As may be seen from the second part of Table I, charged chelate complexes represent but a small segment of the types of ion association complexes used in extraction.

On the symposium are three papers which deal with current developments in the application of both chelate and

ion association extractions to metals analysis. The remainder of the program includes a theoretical paper dealing with the fundamental phase diagram

analysis involved in immiscible solvent pairs and a paper illustrating the novel pair systems and the application of this utilization of solvent extraction as a analysis to choice of suitable solvent valuable adjunct to flame photometry.